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(54) Recovery of Heavy Bitumen in Tar Sands Processing Process

(72) Sethi, Amar J.;
Beardow, Anthony P.,
Canada

(73) Granted to Suncor, Inc.
Canada

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ABSTRACT

Abnormal tar sands containing transitional metals which do not give acceptable bitumen recovery levels when subjected to the usual flotation process are susceptible to significantly improved bitumen recovery by weakening the polar interactions between bitumen and clay minerals in the tar sands. An effective means for improving bitumen recovery is by oxidation or by reduction of the pH of the hot water extraction mass to a pH below 7.5 and addition of alkali metal silicate or posphate solution.

IMPROVED RECOVERY OF HEAVY BITUMEN IN TAR SANDS PROCESSING PROCESS

BACKGROUND OF THE INVENTION

This invention relates to the hot water process for treating bituminous sands, such as Athabasca tar sands, and more particularly to the treatment of those tar sands which when treated in the usual manner do not lend themselves to efficient recovery of bitumen.

Tar sands (which are also known as oil sands and bituminous sands) are sand deposits which are impregnated with dense, viscous petroleum. Tar sands are found throughout the world, often in the same geographical areas as conventional petroleum. The largest deposit, and the only one of present commercial importance is in the Athabasca area in the northeast of the Province of Alberta, Canada. This deposit is believed to contain perhaps 700 billion - 1 trillion barrels of bitumen. For comparison, 700 billion barrels is just about equal to the world-wide reserves of conventional oil, 60% of which is found in the Middle East.

Athabasca tar sand is a three-component mixture of bitumen, mineral and water. Bitumen is the value for the extraction of which tar sands are mined and processed. The bitumen content is variable, averaging 12 wt.% of the deposit, but ranging from 0 to 18 wt.%. Water typically runs 3 to 6 wt.% of the mixture, increasing as bitumen content decreases. The mineral content is relatively constant ranging from 84 to 86 wt.%.

Several basic extraction methods have been known for many years for separating the bitumen from the sands. In the so-called "cold water" method, the separation is accomplished by mixing the sands with a solvent capable to dissolving the bitumen constituent. The mixture is then introduced into a large volume of water, water with a surface agent added, or a solution of a neutral salt in water. The combined mass is then subjected to a pressure or gravity separation.

The hot water process for primary extraction of bitumen from tar sands consists of three major process steps (a fourth step, final extraction, is used to clean up the recovered bitumen for downstream processing.) In the first step, called conditioning, tar sand is mixed with water and heated with open steam to form a pulp of 70 to 85 wt.% solids. Sodium hydroxide or other reagents are added as required to maintain pH in the range 8.0-8.5. In the second step, called separation, the conditioned pulp is diluted further so that separation can take place wherein the bulk of the sand-size mineral rapidly settles and is withdrawn as sand tailings. Most of the bitumen rapidly floats (settles upward) to form a coherent mass known as froth which is recovered by skimming the settling vessel. A third stream may be withdrawn from the settling vessel. This stream, called the middlings drag stream, may be subjected to a third processing step, scavenging. This step provides incremental recovery of suspended bitumen and can be accomplished by conventional froth flotation. These steps are discussed in detail in the literature of tar sands processing.

The conditioning step of tar sands for the recovery of bitumen from tar sands consists of heating the tar sand/water feed mixture to process temperature (180° - 200°F.), physical mixing of the pulp to uniform composition and consistency, and the consumption (by chemical reaction) of caustic to bring the pH of the system to 8.0 to 8.5. Under these conditions, bitumen is stripped from the individual sand grains and mixed into the pulp in the form of discrete droplets of a particle size on the same order of that of the sand grains. The same process conditions, it turns out, are also ideal for accomplishing deflocculation of the clays which occur naturally in the tar sand feed. Deflocculation, or dispersion, means breaking down the naturally occurring aggregates of clay particles to produce a slurry of individual particles. Thus, during conditioning, a large fraction of the clay particles become well dispersed and mixed throughout the pulp. Such a procedure is very effective for efficient recovery of bitumen with about 90% of the tar sands treated. However, about 10% of the tar sands mined do not lend themselves to efficient recovery by such technique. It has been observed that when these abnormal tar sands are treated in the usual manner, the bitumen which would be expected to float in the separation step actually sinks to the bottom and is carried away with the mineral fines as waste. It is an object of this invention to provide a process for efficient bitumen recovery from such heavy tar sands.

BRIEF DESCRIPTION OF THE INVENTION

In accord with this invention it has been found that the abnormal tar sands which contain transition metals, particularly

i1 ., do not lend themselves to the usual conditioning process, but these abnormal tar sands can be efficiently handled for high bitumen recovery by weakening the strong interaction between the bitumen and minerals caused by the metals, which are concentrated in the clays contained in the tar sands. These metals bind the bitumen to the clays through polar interactions (i.e. by Van der Waal type bonding as determined by infra-red spectra) and thus cause the bitumen to be carried down with the clays and minerals. This bond weakening is accomplished by any one of several techniques such as oxidation or, preferably, adjusting the pH of the material to be conditioned to a pH of just below 7.5; e.g. about 7.0 to about 7.4. Subsequent to the pH adjustment, the tar sands material is treated with sodium silicate solution to reduce its viscosity and it is the combination of these steps that results in a high recovery of bitumen from the abnormal tar sands.

DISCUSSION OF PRIOR ART

In the recovery of the bitumen from tar sands a large volume of tailings comprised of hydrocarbon sand and water are sent to waste and, because they cannot be discharged to rivers and streams because of environmental problems, are stored in large ponds. Much effort has been made to treat these tailings for recovery of water and bitumen with numerous techniques being developed. Of interest here is the technique disclosed in Canadian Patent 1,023,677 which teaches the use of carbon dioxide to reduce the pH of tailings in sedimentation reservoirs to a value of about 4.0

.o about 6.0 whereby the chemical bonding between bitumen and mineral particles are broken and the hydrocarbons rise to the surface so that the water may be recycled or put into a natural water course. Although in the present invention the Van der Waal forces between bitumen and minerals are weakened, the use of CO_2 or acid alone is inadequate to permit the successful processing of the bitumen for recovery as the mass becomes too viscous for handling. Thus, the prior art technique of pH reduction to about 4 to about 6 with carbon dioxide as applied to tar sands tailings is not germane to the process of this invention which relates to those peculiar tar sands containing transition metals.

DETAILED DISCUSSION OF THE INVENTION

As indicated above, the conditioning step used in the hot water process for bitumen recovery from Athabasca tar sands using caustic soda to adjust the pH to about 8.5 generally is very effective for about 90% of the tar sands processed. The remaining 10%, however, do not satisfactorily give up their bitumen with such treatment and the bitumen recovery of these abnormal tar sands has been observed to be as little as 25% of the expected amount.

In accord with this invention, it has been established that these abnormal tar sands contain unexpectedly high amounts of transition metals, particularly iron, concentrated largely in the clay content of the tar sands. It has been found that it is when the iron content exceeds about 1.0% that the adverse effect on bitumen recovery is observed. Iron and the other transitional metals in

reduced form are present in the tar sands together with anions such as carboxylates, naphthalates, sulfonates and the like, which effect rather strong bonding between the bitumen and clay. Since the clay is of high density, it carries the bitumen down with it as it sinks to the bottom of the separation vessel and thus bitumen recovery is lowered significantly.

To overcome this phenonemon, the process of this invention weakens this bonding either by a specific oxidation step or by adjusting the pH of the system to a value of below 7.5 (preferably about 7.0 to about 7.45) whereby the polar anions are converted to non-polar free acid groups. However, this pH adjustment alone is insufficient to effect satisfactory commercial separation of the bitumen because the pH adjustment results in a significant increase in viscosity of dispersed clays which adversely affects bitumen separation. Accordingly, it is necessary to reduce the viscosity of the system and this is preferably done by the addition of a viscosity reducing agent such as an aqueous solution of an alkali metal silicate (e.g., sodium silicate) or an alkali metal phosphate (e.g., sodium hexametaphosphate). Upon carrying out the combined steps of pH adjustment and viscosity reduction it is observed that bitumen flotation is significantly enhanced and very high bitumen recovery is achieved.

The pH adjustment of the tar sands material is readily achieved by addition of an acid to the aqueous suspension of tar sands until the system has a pH of just below 7.5. Preferred acids will be hydrochloric, sulfuric, carbonic (or CO_2 gas), phosphoric

and the like. All that is required is that the acid be added with thorough agitation until the desired pH is reached.

The viscosity adjustment step is also easily carried out and is done so that the adjusted pH to below 7.5 is not affected. Preferably, an aqueous solution of sodium silicate (about 40% solids) is added to the aqueous suspension of tar sands so as to provide about 20-50 parts of silicate per million parts of tar sands, but the correct amount is easily ascertained by using viscosity measurement as a control. The desired viscosity for the treated tar sands will be about 1-5 centipoise and the appropriate amount of silicate will be used to achieve this value.

As indicated, the interaction between the bitumen and minerals in abnormal tar sands may be weakened by oxidation, and such oxidation may be carried out in numerous ways. Thus, for example, stockpiling of the tar sands in air and dynamiting the ore body will be an effective oxidation means. Also, introduction of oxidizing agents into the aqueous suspension of tar sands is effective. However, the pH adjustment method discussed above has the advantage of also flocculating the clays present and is the preferred method.

Subsequent to the pH and viscosity adjustment by the method of the invention, the tar sands suspension is handled in the usual manner, the bitumen which floats to the top being separated off, a middlings layer taken for further usual handling and the clay minerals being removed from the bottom of the separator.

The following examples will illustrate the method of the invention.

Example 1

A laboratory batch extraction unit is used to approximate the hot water extraction process of tar sands. In this unit the tar sand sample and water are slurried in a stainless steel pot of the batch extraction unit and the mixture is neutralized and reduced in viscosity. A predetermined amount of flood water is introduced and the floated primary froth retrieved. Further mixing and aeration allows the recovery of secondary froth. Samples of tar sand feed and the recovered froths are submitted for bitumen/water/solids analysis, thus allowing bitumen recoveries to be calculated on an input basis. This apparatus and technique is described by E. C. Sanford and F. A. Seyer, American Chemical Society Division of Fuel Chemistry, Pregenist 23 (4), 54-62 (1978) and by the same authors in CIM Bulletin 72 (803), 164-169 (1979).

The procedure which is used for this example employs one sample which corresponds to the usual extraction procedure, where caustic is added to the conditioning unit to a pH of about 8.0, a second caustic treated sample where the pH is reduced with hydrochloric acid (or CO_2) to a pH just below 7.5 (about 7.45) and a third sample where sodium silicate is also added in an amount of 50 ppm to an acid treated sample (pH about 7.45). The bitumen recoveries in each of these samples using a tar sands containing less than 1% iron and with a tar sands containing more than 1% iron is shown in Table I.

TABLE I

PERCENT RECOVERY OF BITUMEN FROM TAR SANDS CONTAINING IRON

TREATMENT	Iron Content Less than 1% MEAN	Standard Deviation	Iron Content More Than 1% MEAN	Standard Deviation
CAUSTIC TO pH 8.0	91.5	14.7	76.0	23.4
NEUTRALIZATION WITH HCl TO pH 7.45	83.8	18.8	61.2	28.6
NEUTRALIZATION + SODIUM SILICATE	96.4	5.25	85.6	14.0

As can be seen from the table, the bitumen recovery is significantly improved only by adjusting the pH to 7.45 and lowering the viscosity by use of sodium silicate. Also evident from the table is the greater consistency of high recovery which results in a higher level of confidence for the process.

Example 2

Samples of abnormal tar sands which sink to the bottom of the separation vessel during hot water extraction and give poor bitumen recovery are allowed to age in air for about two weeks (e.g., under oxidizing conditions). At the end of the aging period the samples are subjected to extraction and are found to give high recovery of bitumen.

Example 3

When normal tar sands which give good bitumen recovery are soaked in a sodium dithionite solution to subject them to a reducing environment, they become abnormal in the extraction process and sink to the bottom of the extraction vessel, giving poor recovery of bitumen. This process can be reversed either by oxidizing with a hydrogen peroxide solution or by following the procedure of Example 1 with mineral acid and silicate addition.

CLAIMS

Claim 1. In the hot water extraction process for tar sands, the method for improving the recovery of bitumen from tar sands containing transition metals which effect abnormal behavior of said tar sands by causing excessive amounts of bitumen to be carried down with the clay minerals, which method comprises weakening the polar interaction between the bitumen and clay minerals in said tar sands by adjusting the pH of the hot water extraction mass to a pH of just below 7.5 or by oxidation.

Claim 2. The method of Claim 1 wherein the predominant transition metal in said tar sands is iron.

Claim 3. The method of Claims 1 or 2 wherein the weakening of the polar interaction is effected by adjusting the pH of the hot water extraction mass to a pH of just below 7.5 and the viscosity is adjusted to about 1 to about 5 centipoise.

Claim 4. In the hot water extraction process for tar sands, the method for improving the recovery of bitumen from tar sands containing transition metals which effect abnormal behavior of said tar sands by causing excessive amounts of bitumen to be carried down with the clay minerals, which method comprises weakening the polar interaction between the bitumen and clay minerals in said tar sands by adjusting the pH of the hot water extraction mass to a pH of just below 7.5 and the viscosity

is adjusted to about 1 to about 5 centipoise with an alkali metal silicate or phosphate solution.

Claim 5. The method of Claim 4 wherein sodium silicate is added in an amount of about 10 to about 50 ppm.

Claim 6. In the hot water extraction process of tar sands, the method for improving the recovery of bitumen from tar sands containing iron in an amount exceeding about 1.0% which effects abnormal behavior of said tar sands by causing excessive amounts of bitumen to be carried down with the clay minerals, which method comprises adjusting the pH of the hot water extraction mass to a pH between about 7.0 and 7.45 and adding an alkali metal silicate to adjust the viscosity for about 1 to about 5 centipoise.

Claim 7. The method of Claim 6 wherein the pH is adjusted with a mineral acid.

Claim 8. The method of Claim 7 wherein the acid is hydrochloric acid.

Claim 9. The method of Claim 1 wherein the polar interaction is weakened by oxidation.

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Claim 10. The method of Claim 9 wherein the oxidation is carried out by adding the oxidizing agent to the aqueous dispersion of tar sands to be subjected to hot water extraction.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente